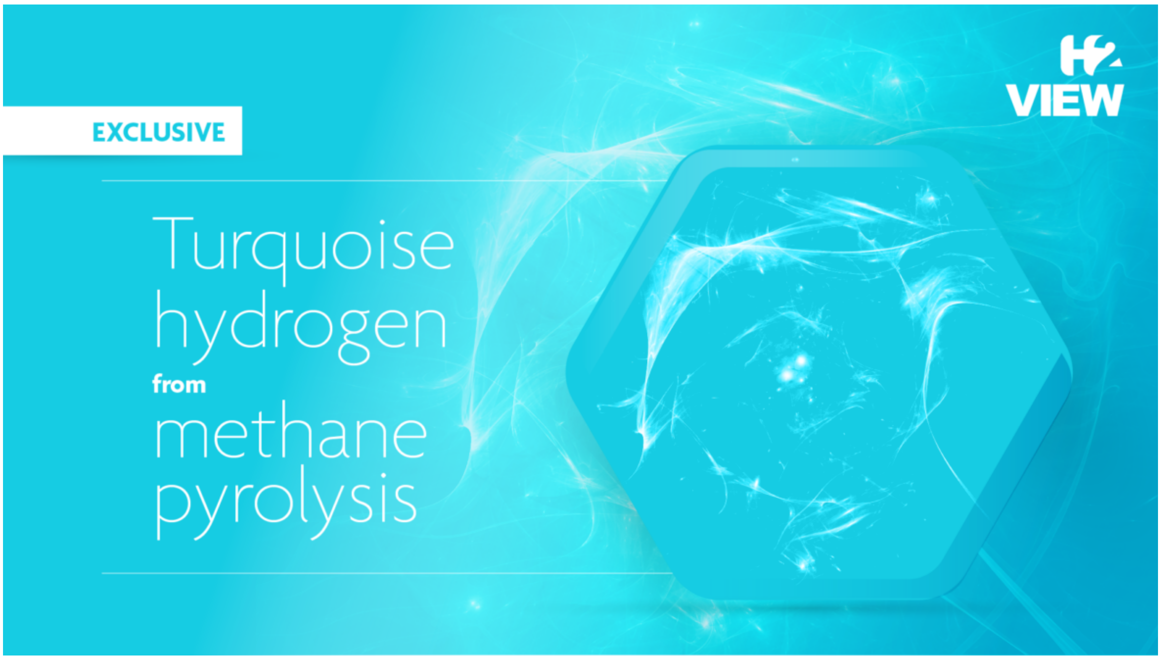


Turquoise hydrogen from methane pyrolysis

By Stephen B. Harrison, Dr. Oliver Borm on Mar 16, 2021 | Translate FEATURE

At present, about 95% of the hydrogen that is produced is derived from fossil fuels using various thermochemical processes. Gasification consumes solids such as petcoke and coal. Other gas-phase reforming processes are fed with methane, naphtha, or refinery gas.

Auto thermal reforming (ATR), steam methane reforming (SMR) and partial oxidation (POX) are the main thermochemical processes in play today. These processes produce syngas which is a mixture of hydrogen and carbon monoxide. Sometimes, two out of the three processes are combined in series to produce the desired ratio of carbon monoxide to hydrogen. If hydrogen is the target gas, carbon monoxide may be reacted with steam and converted to carbon dioxide and hydrogen in a subsequent water-gas shift reactor.

These thermochemical processes produce about 10 kg of carbon dioxide (CO_2) for each kg of hydrogen. If the CO_2 is not captured, the resulting hydrogen is referred to as 'grey' or 'black' hydrogen.

If this hydrogen is used in fuel cell powered cars, with a consumption of about 1kg of hydrogen per 100km, the net result would be emissions of 100 gCO_2/km when upstream emissions are considered. This exceeds the current European fleet emissions target of 95 gCO_2/km. The direct use of compressed natural gas in internal combustion engines would emit less CO_2 from a total system perspective.

Through this example, it becomes clear that hydrogen must be produced at scale as a clean energy vector to mitigate greenhouse gas emissions and combat climate change. The use of carbon capture to mitigate the CO_2 emissions from grey or black hydrogen production to result in blue or purple hydrogen is one option. Green hydrogen produced on electrolysers fed with renewable electrical power is another.

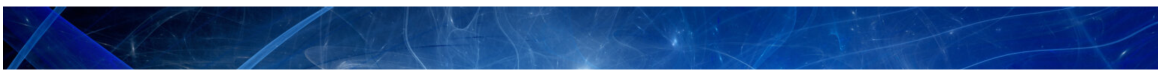
Turquoise hydrogen, produced by methane splitting, also known as methane pyrolysis or cracking, is also a potential pathway to low-carbon hydrogen.

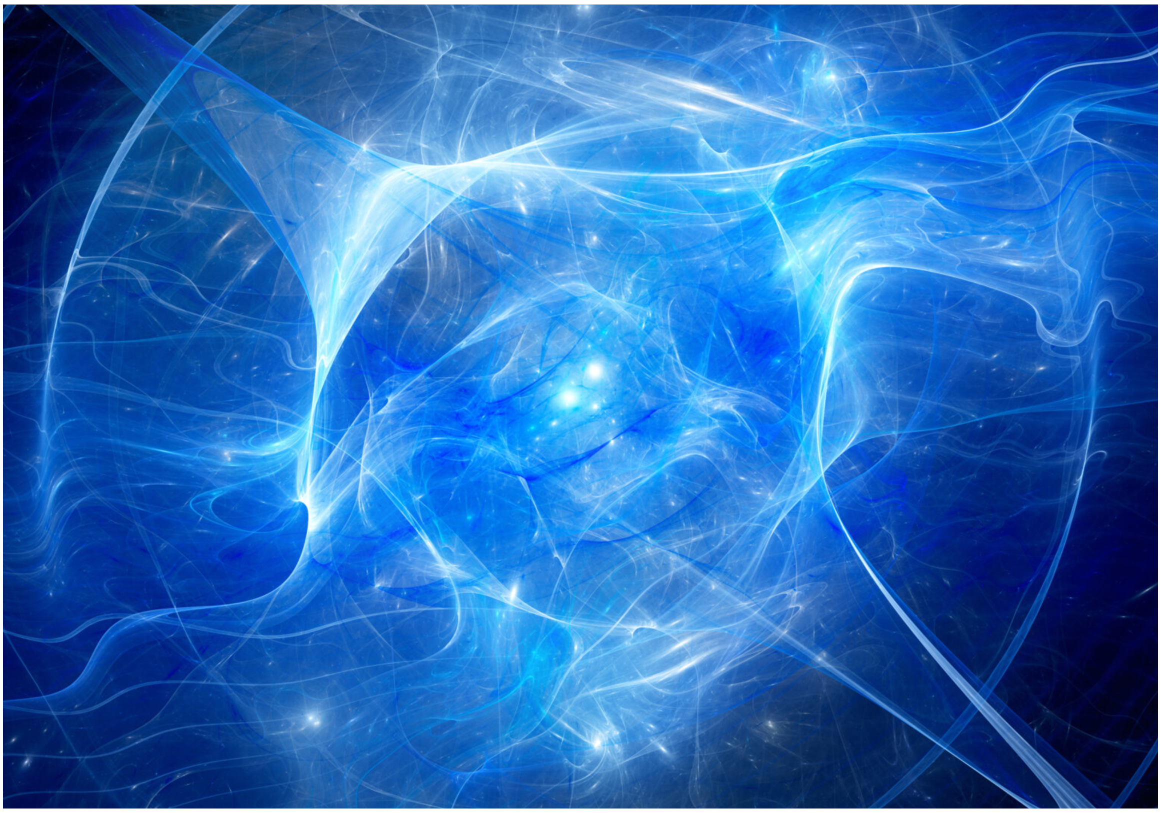
The chemistry of methane pyrolysis

Methane pyrolysis is endothermic, meaning that it requires heat energy to convert methane to hydrogen and solid carbon. The reaction has the chemical formula: $CH_4 \rightarrow C_{(s)} + 2H_2$.

There are different options for the heat supply. Indirect heating using burners fuelled by hydrogen or natural gas as a fuel is one option. Indirect electrical heating or direct heating with an electrical plasma are also possible. These heating modes could use renewable electricity, biomethane or low carbon hydrogen to minimise CO_2 emissions from the process.

Research into methane pyrolysis has been undertaken since the 1960s. In the past 10 years, methane pyrolysis has picked up momentum and several companies have piloted various technologies. Each project has sought to overcome some of the challenges inherent in this process. It is only in the past few years that we have seen commercial operations based on methane pyrolysis emerge as successful business entities.





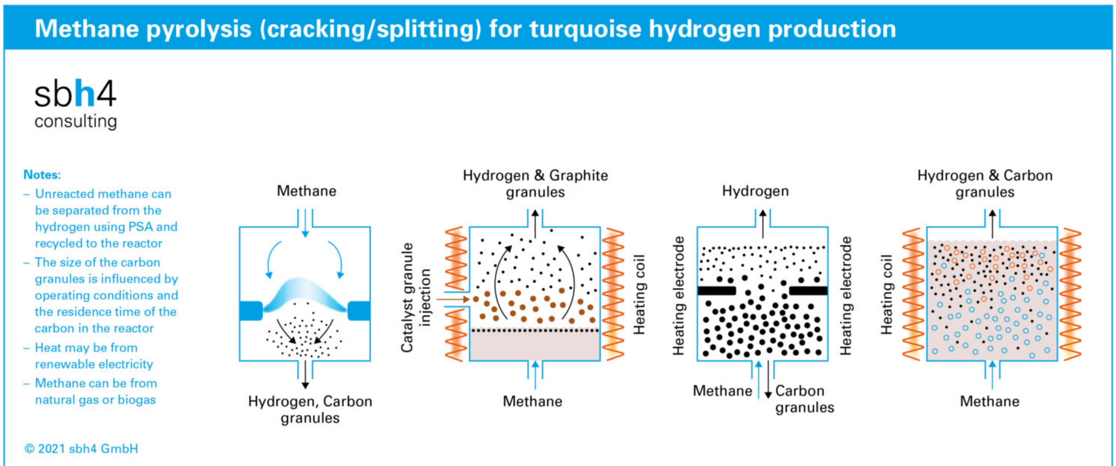
Plasma for methane pyrolysis

Plasma pyrolysis

Monolith Materials started development of its methane pyrolysis process in 2012. Methane is heated by means of renewable electricity to 2,000°C. At this temperature, the methane molecule splits and forms a plasma. This leads to the formation of carbon black, while the protons split off from the methane molecule and recombine to form hydrogen molecules.

At this very high temperature, the reaction takes place without a catalyst. But engineering a system to operate at these temperatures is challenging and careful material selection is essential.

In 2016, construction started on the Olive Creek1 plant at Lincoln, Nebraska in the US. It was commissioned in 2020 and has a production capacity of 14,000 tonnes of carbon and 2,500 tonnes per year of hydrogen. A second plant named Olive Creek2 is planned to have a capacity of 194,000 tonnes of carbon black per year and will produce close to 40,000 tonnes per year of hydrogen.



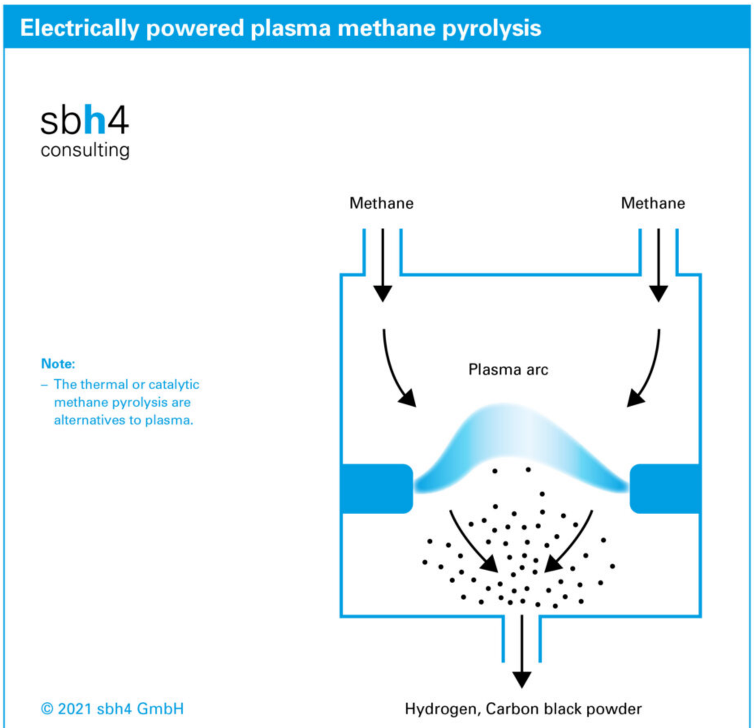
	Plasma Pyrolysis	Fluidised Bed	Moving Carbon Bed	Molten Metal or Molten Salt
Process shown	Monolith Materials	Hazer	BASF	TNO or C-Zero
Hydrogen content at reactor outlet	~95%	~92%	~92%	Up to 95%
Carbon production	Carbon black as powder or granules	80 to 95% graphite encapsulating catalyst dust particles	Carbon black as powder or granules	Carbon black as powder or granules
Catalyst required	No	Iron oxide granules	Carbon bed	Molten 27% Nickel-73% Bismuth Molten Manganese Chloride
Heating mechanism	Direct heating with plasma	Indirect heat applied around the reactor	Electrodes to heat the carbon bed and indirect heat applied around the reactor	Indirect heat applied around the reactor or electrodes to heat the melt in a separate vessel
Reactor temperature	2000 °C	900 °C	1000 to 1400 °C	Depends on melt, 650 to 1100 °C
Reactor pressure	Close to atmospheric pressure	Close to atmospheric pressure	Close to atmospheric pressure	Up to 5 bar

Moving carbon bed thermal process

From 2013-2017, a lab-scale reactor was built and operated by BASF at Ludwigshafen, Germany. It identified key process parameters and construction of a larger pilot plant soon followed. Both projects were supported by the BMBF (German Federal Ministry of Education and Research).

In the BASF process, external electrical heating to 1000°C is used to drive the pyrolysis reaction. Since the heating is electrical, the process could use renewable energy. The reactor vessel is a vertical cylinder. Methane enters at the base and flows upwards through a downward-moving bed of solid carbon granules. The methane decomposes to form carbon that binds to the bed of carbon granules and hydrogen gas. Hydrogen and unreacted methane rise to flow from the top of the reactor vessel. Solid carbon leaves from the lower part of the column.

The reactor is heated to drive the endothermic pyrolysis reaction and to combat heat losses that result as the hot hydrogen gas and solid carbon products leave the reactor. Heat recovery for energy efficiency is an essential aspect of all thermochemical hydrogen production processes. SMRs and ATRs use large heat exchangers to recover heat from the process which can generate steam and warm up the incoming gases. To make pyrolysis efficient, efficient heat recovery mechanisms must be developed and implemented on commercial systems.



	Plasma Pyrolysis of Methane (Methane Cracking, Methane Splitting)
Carbon feedstock	Methane from natural gas
Target chemical reactions	$CH_4 \rightarrow C + 2H_2$
Additional side reactions	$2CH_4 \rightarrow C_2H_2 + 3H_2$
Carbon produced as	Carbon black powder
Product gas pressure	Close to atmospheric pressure
Product gas temperature	1500 to 2000 °C

Fluidised bed catalytic process

Hazer has operated a fluidised bed methane pyrolysis reactor pilot plant in Kwinana, Western Australia since 2016. Work has commenced on planning a commercial-scale demonstration plant.

In the Hazer process, a fluidised bed reactor is externally heated to 900°C. Iron oxide powder is injected to act as a catalyst. Methane gas is introduced from the bottom of the reactor. As the methane molecule splits, carbon atoms form graphite on the catalyst surface and hydrogen is released. The upward flow of hot gases carries the low-density graphite particles out of the top of the reactor.

The graphite exits the reactor together with the hydrogen and any unreacted methane. The methane and hydrogen are separated, and the methane is recycled into the reactor. The graphite-coated catalyst dust can be processed to produce functional materials.

Molten-metal catalysed methane bubble reactor

In molten metal methane pyrolysis, methane gas is bubbled upwards through a column of molten metal which is a catalyst to convert methane to carbon and hydrogen. The process has been researched extensively as part of the EMBER project at TNO in the Netherlands. It is also being considered by some Russian natural gas producers, such as Gazprom, for turquoise hydrogen production.

The technology was initially developed in combination with research into potential future Generation IV nuclear power plants. Numerous papers have been published in the past two decades and molten metals such as magnesium and tin have been used. Most recently, a nickel/bismuth molten metal mixture has been found to have high potential. Nickel is one of the predominant metals used in gas-phase reforming catalysts. Despite recent progress, commercialisation of this process is not anticipated during this decade.

Molten salt catalysed methane bubble reactor

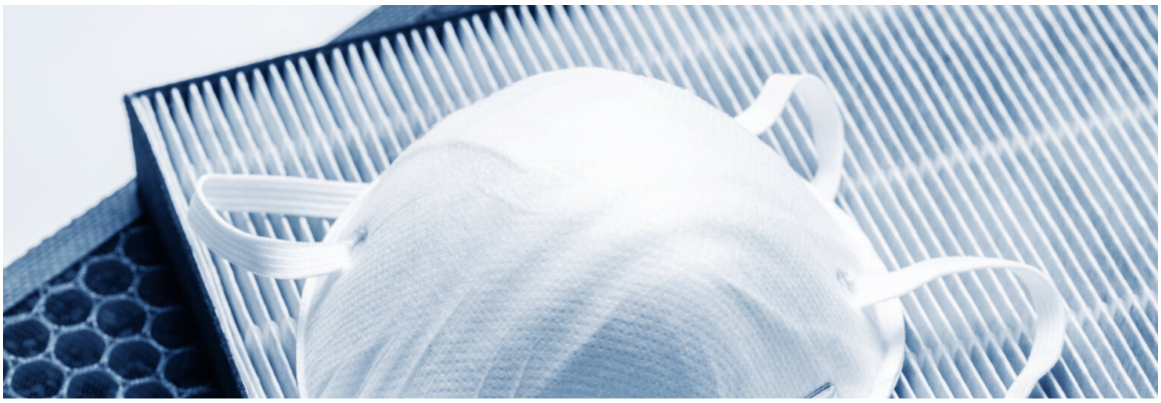
A challenge of the molten metal bubbler reactor is separation of the solid carbon from the molten metal at the top of the reactor. TNO has innovated a solution to this issue by floating a layer of molten salt on top of the molten metal.

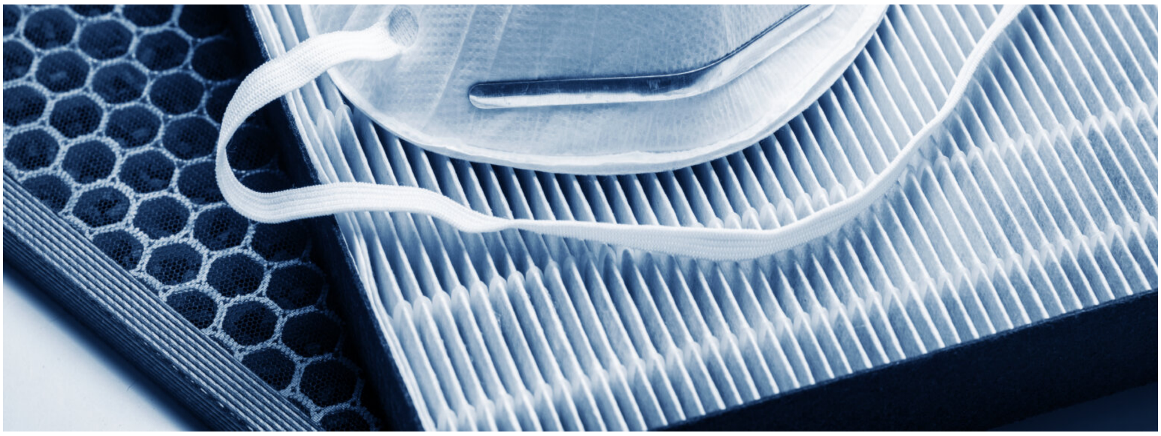
Other researchers have resolved the problem by replacing the molten metal with a molten salt in the entire bubble column. In California, C-Zero has experimented with this process and has determined that manganese chloride is a particularly effective catalyst for methane splitting.

Carbon utilisation and carbon neutrality

A question that arises from methane pyrolysis with hydrogen as the target is: what happens with the various forms of solid carbon that are produced?

Graphite, carbon black and activated carbon are used in various applications. Carbon black powder is a filler material in tyres and consumer goods such as the plastics for cell phones and computers. Activated carbon is a filter for gases and water to remove harmful pollutants. Graphite is used to produce electrodes for gold, silver, steel, and aluminium processing.





If turquoise hydrogen production becomes a mainstream pathway to hydrogen, the amount of solid carbon produced will greatly exceed demand from current applications. If carbon black becomes abundant at low cost, it might find additional application as a soil-improver in agriculture or as a substitute for coke in ironmaking.

Turquoise hydrogen production has the potential to be carbon negative if it is fed with biomethane and renewable power is used for heating or to generate the plasma. To determine whether methane pyrolysis has a net positive, negative, or neutral effect on greenhouse gas emissions and climate change, a complete Life Cycle Analysis (LCA) is required. This investigates the holistic cycle of carbon usage, ranging from production though usage to subsequent product recycling or disposal.